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Engaging visible light-induced triplet sensitization towards intramolecular [4+2] cycloadditions of naphthalenes and quinolines†

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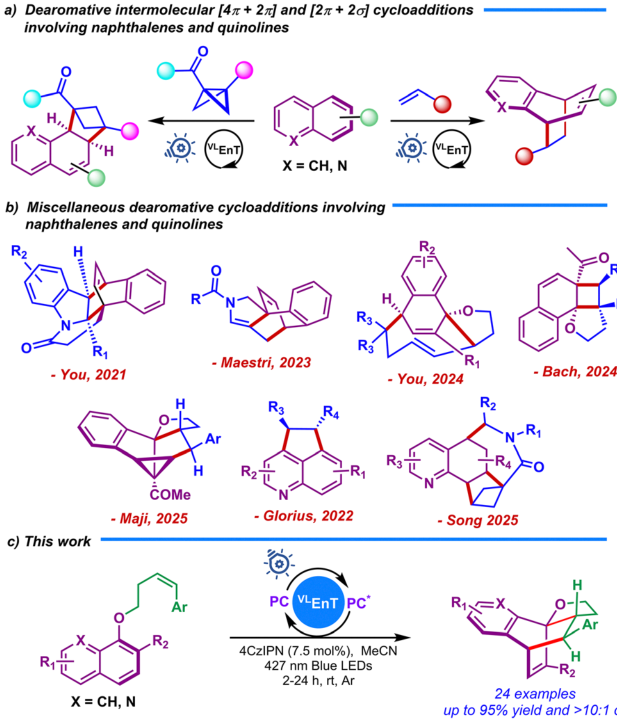
Herein, we report the visible light-promoted intramolecular [4+2] cycloadditions of alkene-tethered naphthalenes and quinolines by employing a metal-free photocatalyst. The endeavor leverages the triplet sensitization of the designed substrates to give a wide range of monoxolane-bearing 3D scaffolds in high yields and selectivities. The appended mechanistic studies elucidate the proposed reaction pathway that involves triplet energy transfer catalysis.

Congruent with the modern-day upsurge towards greener and sustainable catalysis, the employment of photons as a traceless energy source is highly commendable and has paved the way for the renaissance of photocatalysis.[1] Visible light-mediated triplet energy transfer (^{VL}EnT) sensitization has evolved as the savior of essential problems such as poor yields and detrimental chemo-, regio-, and stereoselectivities. With an astute choice of photosensitizers (PSs), achieving the targeted molecular complexity *via* substrate sensitization becomes feasible.[2]

The exploration of dearomative cycloadditions under this regime has embraced specially decorated (hetero)aromatic substrates for facilitating energy transfer (Scheme 1a).[2b,3] The employment of specific solvent systems or activating Lewis acid additives has been helpful in achieving extraordinary reactivity during these cycloadditions.[3e,4] A thorough survey of the recent works showcases the dominance of naphthalene- and quinoline-based systems in the emerging field of ^{VL}EnT-based cycloadditions.[5] Recent works from Maji, Brown, Jiang, and You have incorporated naphthalenes towards intermolecular [4+2] and [2+2] cycloadditions *via* ^{VL}EnT.[3c,6] Similarly, Maestri and You have taken advantage of the pendant naphthalene affixed to the (hetero)aromatic core to perform selective dearomatization.[7]

More recent advancements include unprecedented [2+2], [3+2], and [5+4] cycloadditions in naphthalenes by Bach, Maji, and You, respectively (Scheme 1b).[8] Needless to mention, azaarenes have been targeted by the scientific community since the inception of ^{VL}EnT for producing aesthetic and pharmacologically relevant 3D architectures.[9] Suitably decorated quinolines have been implemented for dearomative [4+2] and [2+2] cycloadditions with alkenes, *peri*-[3+2] cycloadditions with alkynes, and strain release [2π+2σ] cycloadditions with bicyclo[1.1.0]butanes (BCBs) under thoroughly screened reaction parameters (Scheme 1b).[3e,4,10]



Scheme 1 (a, b) State-of-the-art photocatalytic dearomatization strategies and (c) this work.

We herein report the intramolecular [4+2] cycloaddition *via* ^{VL}EnT utilizing pendant alkene-bearing *O*-tethered naphthalenes and quinolines by leveraging the entropic advantage of the diene and dienophile components being sutured together, which to the best of our knowledge has not been reported with visible light EnT catalysis (Scheme 1c). The endeavor presents a

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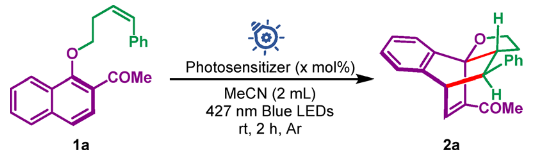
Table 1 Key reaction optimization and control experiments[a]



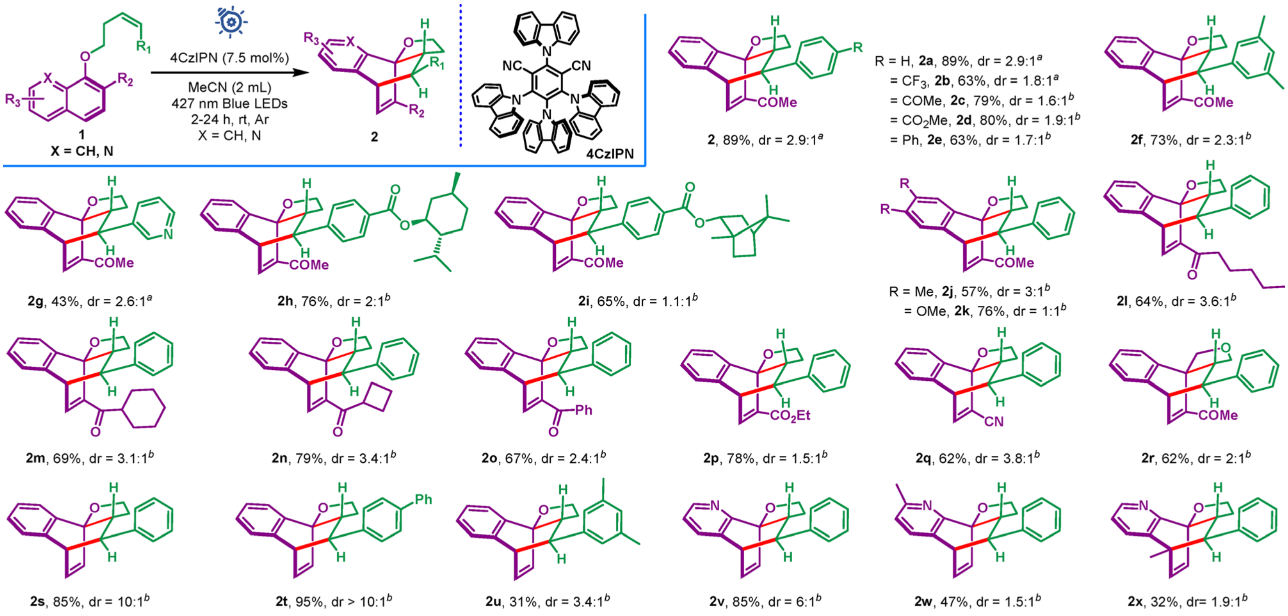
Entry	Photosensitizer (x mol%, E_T)	% yield (dr)
1	4CzIPN (7.5 mol%, 53 kcal mol^{-1})	89 (2.9 : 1)
2	Rose Bengal (10 mol%, 42 kcal mol^{-1})	< 5
3	EOSIN Y (10 mol%, 44 kcal mol^{-1})	< 5
4	$Ru(bpy)_3(PF_6)_2$ (1 mol%, 46.5 kcal mol^{-1})	< 5
5	$[Ir(ppy)_2(dtbbpy)]PF_6$ (1 mol%, 49.2 kcal mol^{-1})	62 (2.7 : 1)
6	4DPAIPN (10 mol%, 59.3 kcal mol^{-1})	68 (2.7 : 1)
7	CH_2Cl_2 instead of MeCN	85 (1.5 : 1)
8	THF instead of MeCN	65 (1.7 : 1)
9	4CzIPN (5 mol%)	69 (2.9 : 1)
10	4CzIPN (10 mol%)	71 (2.7 : 1)
11	4CzIPN, 1 h reaction	57 (3 : 1)
12	4CzIPN, 3 h reaction	80 (2.8 : 1)

Reaction conditions: **1a** (0.1 mmol), photosensitizer (1–10 mol%), MeCN (2 mL), blue LED irradiation under N_2 at rt, 2 h. [a] The yield and *endo* : *exo* ratio were determined by ^1H NMR analysis using trimethoxy benzene as an internal standard.

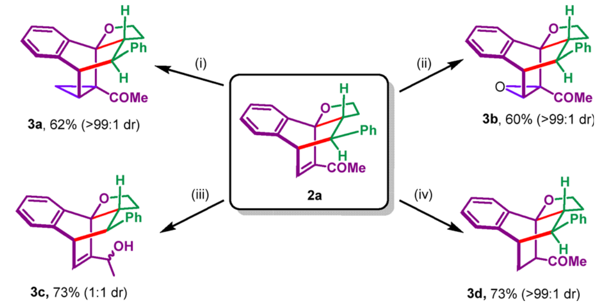
library of tetrahydrofuranyl moiety-bearing polycyclic monoxolanes with potential pharmacoactivity. The designed protocol utilizes the well-known organic photocatalyst 4CzIPN, thus being an entirely metal-free and greener catalytic venture.

We initiated our investigation using **1a** as the model substrate (Table 1). A systematic screening of commercially available photosensitizers (PSs) was performed on a 0.05 M solution of **1a** in acetonitrile under irradiation with blue light-emitting diodes (LEDs). The optimum result was achieved employing 4CzIPN (7.5 mol%, E_T = 53 kcal mol^{-1}), which afforded an 89% yield of the targeted [4+2]-cycloadduct **2a** after 2 h under 427 nm light irradiation, with a 2.9 : 1 diastereomeric ratio (dr) favoring the *endo* diastereomer (entry 1). Photosensitizers with lower E_Ts proved less effective for this transformation (entries 2–4). $[Ir(ppy)_2(dtbbpy)]PF_6$ and 4DPAIPN gave the cycloadduct **2a** in 62 and 68% yields, respectively, with almost unwavering dr (entries 5 and 6). Other PSs with higher E_Ts gave a mixture of [4+2]- and [3+2]-cycloadducts.[8a] Dry and degassed acetonitrile was found to be optimal for the targeted cycloaddition, while the other organic solvents resulted in poorer yields and dr (entries 7 and 8). Similar observations were made upon changing the 4CzIPN loading (entries 9 and 10). In these cases, 25% and 13% of **1a** remained unreacted, respectively. Time optimizations showed that reactions set for shorter or longer durations than two hours resulted in lower yields (entries 11 and 12). Further details of the reaction optimizations are tabulated in Tables S1–S7 (ESI†).

To evaluate the versatility of this protocol, we explored a diverse range of 2-acylnaphthalenes tethered to alkenes with varying electronic and steric properties (Scheme 2). The reactions proceeded smoothly, delivering the corresponding [4+2]-cycloadducts **2a–i** in 43–89% yields with modest diastereoselectivities. Notably, the methodology tolerated a variety of functional groups, including CF_3 (**2b**), COMe (**2c**), CO_2Me (**2d**), and Ph (**2e**). Furthermore, substrates incorporating a pyridyl moiety (**2g**) and bioactive scaffolds such as menthol (**2h**) and borneol (**2i**) were successfully transformed to their sp^3-rich cycloadducts, underscoring the synthetic utility of this approach. The scope was further extended to 6,7-disubstituted naphthalenes (**2j** and **k**), which reacted with comparable efficiency. Additionally, 2-acylnaphthalenes featuring linear alkyl (**2l**), cyclic alkyl (**2m** and **n**), and phenyl (**2o**) substituents underwent smooth cycloaddition, affording products in 64–79% yields with diastereoselectivities up to 3.6 : 1 dr. Substrates with 2-carboethoxy (**2p**) and 2-cyano (**2q**) groups were also compatible. A carbon-tethered substrate proved equally viable, furnishing the cycloadduct **2r** in 62% yield and 2 : 1 dr.



Scheme 2 Substrate scope. Reaction conditions: Table 1, entry 1. Combined NMR yields have been provided, and the *endo* : *exo* ratios have been determined from crude NMR analysis. Isolated yields for the substrates are available in the ESI.† [a] Time: 2 h; [b] time: 24 h.

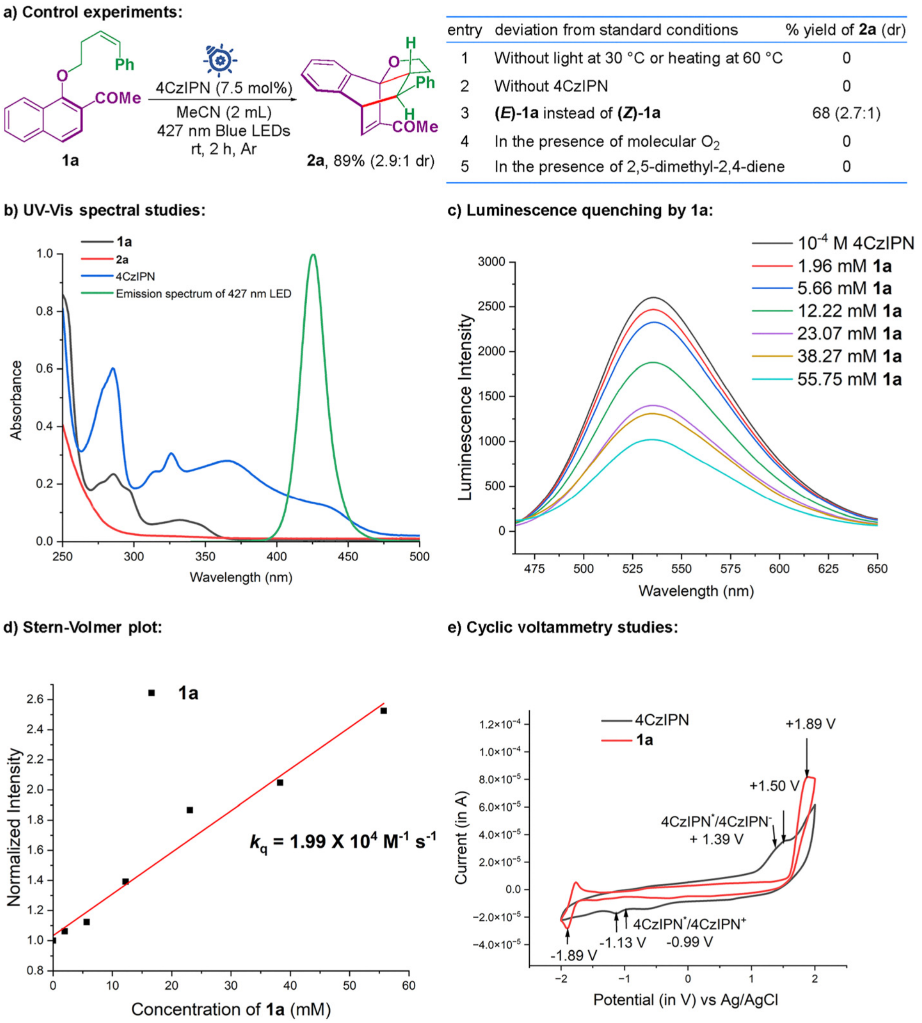


Scheme 3 Post-synthetic transformations. Reaction conditions: (i) **2a** (0.1 mmol), NaH (0.12 mmol), trimethylsulfoxonium iodide (0.12 mmol), DMSO (1 mL), rt, 24 h; (ii) **2a** (0.1 mmol), H_2O_2 (30% aq. solution) (0.3 mmol), NaOH (0.015 mmol), MeOH (0.5 mL), 0 °C–rt, 10 h; (iii) **2a** (0.1 mmol), $CeCl_3{\cdot}7H_2O$ (0.11 mmol), $NaBH_4$ (0.11 mmol), MeOH (1 mL), 0 °C–rt; (iv) **2a** (0.15 mmol), $ZnCl_2$ (0.075 mmol), Ph_2SiH_2 (0.38 mmol), $Pd(PPh_3)_4$ (0.003 mmol), $CHCl_3$ (2.5 mL), rt, 24 h.

Unlike the previous reports on ^{VL}EnT-mediated [4+2] cycloaddition of naphthalenes,[6b,6c,11] the intramolecular reactions were not dependent on electron-withdrawing functionalities at the β-position of the naphthalene core. Even the parent naphthol-derived substrates (**2s–u**) participated effectively, yielding cycloadducts in up to 95% yield with excellent 10 : 1 dr. Remarkably, the protocol also applied to alkene-tethered quinolines (**2v–x**), further demonstrating its broad utility across diverse (hetero)aromatic systems.

We then performed a few post-synthetic modifications of the cycloadducts to elaborate their synthetic potential (Scheme 3). The Corey–Chaykovsky cyclopropanation of **2a** afforded the corresponding cyclopropane product **3a** as a single diastereomer. H_2O_2–NaOH-mediated epoxidation proceeded smoothly, giving the desired oxirane **3b** in 60% yield and >99 : 1 dr. Cerium(III) chloride/$NaBH_4$ mediated Luche reduction of **2a** gave alcohol **3c** in 73% yield with 1 : 1 dr. Finally, $Pd(PPh_3)_4$ and diphenyl silane-promoted selective reduction of the double bond afforded **3d** in 73% yield with >99 : 1 dr.

Next, control experiments and mechanistic studies were performed to elucidate the reaction mechanism (Fig. 1). No desired [4+2]-cycloadduct was detected without light and under thermal



entry	deviation from standard conditions	% yield of **2a** (dr)
1	Without light at 30 °C or heating at 60 °C	0
2	Without 4CzIPN	0
3	**(*E*)-1a** instead of **(*Z*)-1a**	68 (2.7:1)
4	In the presence of molecular O_2	0
5	In the presence of 2,5-dimethyl-2,4-diene	0

Fig. 1 Mechanistic studies. (a) Control experiments. (b) UV-visible spectra showing 4CzIPN as the sole absorbing species under 427 nm irradiation. (c) Luminescence quenching of a 10^{-4} M solution of 4CzIPN by **1a**. (d) Stern–Volmer plot. (e) Cyclic voltammograms of 4CzIPN and **1a** to validate the proposed triplet energy transfer.

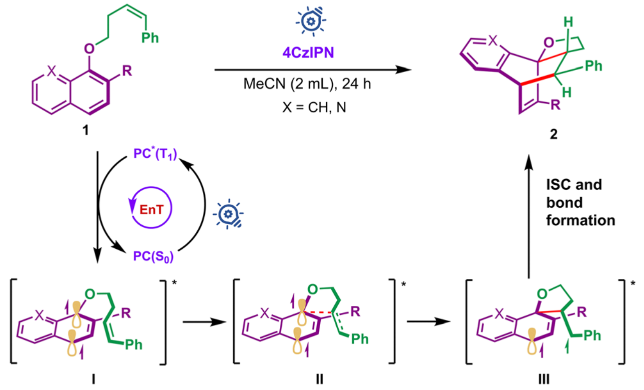


Fig. 2 Proposed reaction mechanism.

exposure of **1a** at 60 °C, negating the possibility of thermal cycloaddition reactions (Fig. 1a, entry 1). UV-Vis spectral studies showed that 4CzIPN is the only 427 nm LED absorbing species (Fig. 1b). Accordingly, the irradiation of the MeCN solution of **1a** at 427 nm without 4CzPN led to its >95% recovery (Fig. 1a, entry 2). The Stern–Volmer analyses revealed the effective luminescence quenching of 4CzIPN by the substrate **1a** with the quenching constant $k_q = 1.99 \times 10^4\ M^{-1}\ s^{-1}$ (Fig. 1c and d). These studies underscore the critical importance of triplet sensitization for the success of the designed protocol. The geometry of the tethered olefin had a trivial influence on the reaction yield and diastereoselectivity (Fig. 1a, entry 3), suggesting the naphthalene ring is responsible for quenching the excited photocatalyst.

Furthermore, the cyclic voltammetry studies helped in negating the possibility of any electron transfer between the substrate and the photocatalyst (Fig. 1e). The redox potentials of the model substrate **1a** lie beyond the redox range of the acetonitrile solution of 4CzIPN in its ground and excited states. The presence of triplet quenchers such as molecular O_2 and 2,5-dimethylhexa-2,4-diene suppressed the reaction entirely, further suggesting the existence of EnT from the excited state PS and the substrate (Fig. 1a, entries 4 and 5).

The reaction pathway for the envisioned intramolecular [4+2] dearomative cycloaddition reaction is proposed in Fig. 2. Upon irradiation, 4CzIPN is excited to its triplet-excited state. Subsequent triplet energy transfer to **1** generated the 1,4-diradical species **I**. The intramolecularly tethered alkene traps the latter to produce the diradical species **III**, where the stability is attributed to the radical positioning at the benzylic sites. Intermediate **III** undergoes intersystem crossing, followed by C–C bond formation to yield the desired [4+2] cycloadduct **2**.

In summary, we developed a milder strategy for dearomatizing stable polycyclic aromatic hydrocarbons using visible light-induced triplet-sensitized cycloaddition of intramolecularly tethered naphthalenes and quinolines. This protocol produces tetrahydrofuranyl-based polycyclic scaffolds with good to excellent yields and moderate diastereoselectivities. Careful screening of photosensitizers and reaction parameters was crucial. Mechanistic studies confirmed the visible light-induced EnT pathway. The method was extended to substrates with diverse properties, and successful post-synthetic transformations were demonstrated, highlighting the protocol's versatility and applicability.

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Conflicts of interest

There are no conflicts to declare.

Data availability

The data supporting this article have been included as part of the ESI.†

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